AlkyClean® Technology

An Inherently Safer Alkylation Technology for the Production of Motor Gasoline Alkylate

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RECENT MILESTONES

- ACS Affordable Green Chemistry Award Winner in 2010 for the development of the AlkyClean process.
- Two U.S. Patents recently issued for AlkyClean technology: 7,875,754 (01/25/2011) for increasing alkylate yield, and 8,163,969 (04/24/2012) for improved catalyst.
- World's first safe and successful start-up of a commercial scale, 2,700 barrels per day, solid catalyst alkylation unit (AlkyClean) on August 18, 2015, at Zibo Haiyi Fine Chemical Co., LTD (Haiyi), Shandong Province, Peoples Republic of China.

SIGNIFICANT U.S. COMPONENT

- Engineering design of the AlkyClean Demonstration Plant at Porvoo (operating between 2002-2004) was executed by ABB Lummus Global, Bloomfield, N.J. (now CB&I). Albemarle's Houston, Texas, plant produced the main component of the catalyst, the zeolite, for the demonstration plant.
- The basic engineering design package for, and commissioning of, the commercial plant at Zibo Haiyi was executed by personnel from the CB&I offices in Houston, Texas.

FOCUS AREAS

Area 2: Replacement of hazardous liquid acid catalyzed alkylation processes (i.e., HF and H_2SO_4) by a true solid acid zeolite catalyst process that has significantly less impact on human health and the environment.

Area 1: Greener synthetic pathway to produce motor gasoline alkylate by a novel harmless catalyst.

NOT ELIGIBLE FOR THE ACADEMIC OR SMALL BUSINESS CATEGORIES

ABSTRACT

Refinery alkylate is an ideal clean gasoline blend component that is produced from light olefins and isobutane. It consists of clean combusting isoparaffins, having both low vapor pressures and very high octane numbers. Furthermore, it contains no environmentally unfriendly or toxic components, such as aromatics, olefins, or sulfur compounds. For compliance with ever stricter environmental regulations, alkylate is the preferred gasoline blending component.

The problem for refineries today is that alkylate production, currently about 30 billion gallons/yr worldwide (60% of which is located in North America), requires the use of liquid acid catalyzed processes (HF or H_2SO_4). HF is extremely toxic and, upon release,

forms clouds that can be lethal up to five miles. Sulfuric acid technologies generate huge quantities of corrosive spent acid, on the order of 10-20 billion lbs/yr, that have to be transported and regenerated, thereby, introducing risk into surrounding communities and adding to the generation of environmentally unfriendly emissions.

For more than 40 years, academic and industrial scientists have been trying to replace these liquid acid technologies by a much greener solid acid catalyst technology. AlkyClean technology is now available and has been commercialized. It is inherently safer to operate and has a lower environmental impact than alternative technology because it employs a true solid catalyst.

This breakthrough has been demonstrated by the successful start-up of the commercial scale (2,700 BPD) plant at Zibo which has met or exceeded all performance expectations. The design basis for Zibo was developed at the Neste Porvoo plant which operated for two years. During this demonstration, the technology was optimized and fully proven for commercial application. Product quality is on par with existing technologies. Moreover, production of waste products like acid soluble oils or spent acids is eliminated, and there is no need for product post-treatment of any kind.

EXECUTIVE SUMMARY

Alkylate, the product of the reaction of isobutane with light olefins (C_3-C_5), is highly valued as an ideal "clean fuels" blending component for the gasoline pool because it has no olefins, carcinogenic benzene or other aromatic compounds, a low sulfur content, a limited heavy end, a low vapor pressure and both high research and motor octane numbers. Currently about 30 billion gallons/yr of alkylate are produced worldwide, 60% of which is located in North America.

Refiners now have available a cleaner and inherently safer alkylation technology, the AlkyClean alkylation process. Based on more than two (2) years of successful operation of the prototype, CB&I successfully scaled it up to commercial scale at Zibo. Other solid acid technologies have only been investigated on much smaller pilot scale and/or still use leachable corrosive components, such as halogens. AlkyClean is the only solid acid technology that is in commercial operation.

The new solid acid catalyst (SAC) process produces high quality alkylate without the drawbacks of the existing hydrofluoric (HF) and sulfuric (H_2SO_4) acid based technologies. Neither acid soluble oils, nor spent acids, are produced, and there is no need for product post-treatment of any kind. It is estimated that about 10-20 billion lb/yr of spent sulfuric acid is being transported and regenerated just for alkylation. Besides these processing advantages, eliminating the use of these toxic and corrosive liquid acids greatly reduces maintenance and monitoring requirements while reducing environmental and personnel safety concerns. Benchmarking efforts have confirmed the overall competitiveness of the new technology.

Central to the new technology is the utilization of a novel, “true” SAC with a patented pore distribution. In this situation, “true” SAC means that the catalytic acid function is intrinsic to the solid itself rather than being a separate component, such as an immobilized liquid deposited on a solid substrate. The formulation is zeolite based. It contains no halogens, has acid sites with optimum strength for alkylation, yields high quality alkylate and exhibits the required activity, stability and regeneration capability necessary for a successful and viable process.

The AlkyClean process has proven to be robust, requiring minimal maintenance, while producing high quality product. The zeolite based solid acid catalyst has exhibited tolerance to both upsets and exposure to contaminants. The catalyst’s ability to be easily and repeatedly regenerated, under mild non-oxidative conditions, with full activity recovery, has been demonstrated over long periods of operation. With all of its very positive benefits, this breakthrough technology provides a profitable addition to the processing portfolio of refiners, as they strive to meet regulatory-driven demand for both cleaner fuels and greener/ safer refining processes.

I DESCRIPTION OF PROBLEM

Currently worldwide about 30 billion gallons per year of alkylate is produced by the reaction of isobutane with C_3 and C_4 olefins, mainly from FCC (Fluid Catalytic Cracking) units. The mixture of multi-branched, gasoline-range hydrocarbons that is formed is an excellent clean gasoline blending stock that can be used to replace toxic and carcinogenic aromatic compounds in the refinery gasoline pool.

However, the currently available liquid acid catalyzed HF and H_2SO_4 processes have many drawbacks. Both acids can inflict serious injury via skin contact and/or inhalation. This increases safety risks for operating personnel and nearby communities. Over the years many incidents have occurred, causing injuries as well as fatalities.

In the case of HF units, leaks may lead to the formation of aerosol clouds that can spread lethal doses of HF upwards of five miles. Based on refinery risk management plans, in the U.S. alone, more than 17 million people currently live within such danger zones (USPIRG: Needless Risk Study, 2005). While mitigation options have been developed, they can be very costly, and have not been universally adopted. Significant risks still exist, especially during unit repair and maintenance or process accidents at adjacent units.

In the case of sulfuric acid, worldwide consumption by alkylation units is in the order of 10-20 billion pounds per year. Regeneration of spent sulfuric acid is carried out by incineration. This consumes energy, produces greenhouse gasses, and also increases the risks of SOx emissions. In addition to the hazards described above, both conventional liquid acid processes require removal of residual acid from the products by scrubbing, washing and neutralization with caustic and/or lime. This leads to the production of waste water and sludge.

Altogether, the incentive to develop and commercialize an environmentally friendly, solid acid catalyst (SAC) alkylation process is very high. Although there have been many attempts during the past 40 years, nobody had of yet succeeded in demonstrating such a technology. Prior approaches have in most cases failed because of poor product selectivity and/or excessively rapid catalyst deactivation, coupled with the lack of an acceptable catalyst regeneration procedure. Also in many cases the catalyst utilized leachable corrosive components such as halogens, trifluorosulfonic (triflic) acid, BF_3 and H_2SO_4, which could migrate into product streams.

Albemarle Catalysts and ABB Lummus Global (now CB&I) started a co-operation in 1996 to develop a catalyst/ process combination that addresses the aforementioned problems. Commercial success was ultimately proven and demonstrated with the start-up of the Zibo plant in August 2015.

II CHEMISTRY OF ISOBUTANE ALKYLATION

In literature, many papers address the chemistry of alkylation (e.g. Catal. Rev.-Sci. Eng., 35(4), p.483-570, 1993). The preferred alkylation products are C_8 trimethylpentanes (TMP), which are formed by the primary reaction of isobutane with butenes. The research octane number (RON) of the various TMP isomers is about 100-110. However, depending on the process and operating conditions, part of the C_8s formed will be dimethylhexanes (DMH), which have a RON of only about 50-60. Also C_5-C_7 (lights) and C_9+ ("heavies") secondary products are formed, which have a lower RON and/or a higher vapor pressure than the favored TMP products.

It is desirable that a catalyst/process combination leads to high TMP/DMH ratios and low by-product formation. Therefore, an understanding of the reaction mechanism is essential for the development of a good SAC process technology. A generally accepted proposal for the mechanism of butene alkylation is presented in Figure 1.

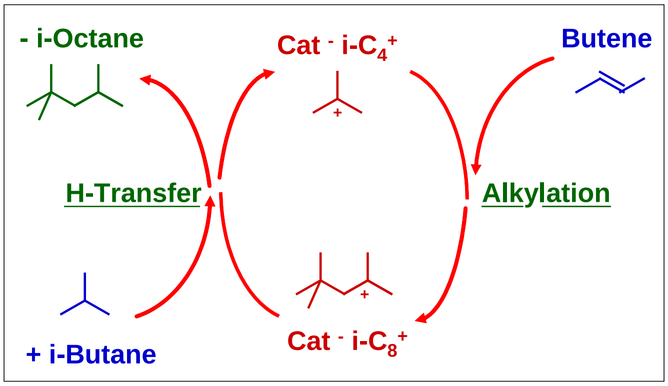

Figure 1. Chemistry

The initial reactions lead to the formation of C_4^+ ions on the acid sites of the catalyst. After reaction with C_4 olefins, C_8^+ ions are formed, which can escape from the catalytic sites after hydrogen transfer reaction with isobutane. In this way, the preferred species, (isooctanes) are produced and C_4^+ ions are formed again. This catalytic cycle can be repeated many times. However, C_8^+ ions can also react with a second olefin, leading to C_{12}^+ ions. The C_{12}^+ ions can "escape" by hydrogen transfer or react further to form higher molecular weight products. Some larger carbonium ions will split into smaller fragments, leading to the formation of the undesired C_5-C_7 and C_9+ compounds. It is clear that high isobutane-to-olefin ratios (I/O) in the reactor feed and high hydrogen transfer reaction rates favor the formation of C_8s over C_5-C_7 and C_9+ compounds.

However, the rate constant of alkylation reactions leading to undesired long chain molecules is about three orders of magnitude higher than the rate constant of hydrogen transfer reactions. Thus, to achieve our product quality goals, the catalyst, reactor and process design should be directed to maximize hydrogen transfer reactions and to attain high I/O at the acid sites.

III PROCESS AND CATALYST DEVELOPMENT AND COMMERCIALIZATION

Attempts to apply SAC in the past failed, because the catalyst and process conditions used resulted in very rapid deactivation of the catalyst. So, in addition to a novel catalyst and a novel reactor and process design, novel regeneration procedures had to be developed.

Catalyst

After pre-screening in a micro reactor, a true SAC was selected. The zeolite used is of a type well proven in industry. However, we had to optimize its strength and the number of acid sites to enhance hydrogen transfer reactions over multiple alkylation reactions. The catalyst particle size and porosity also needed to be optimized using a pilot plant that allowed the investigation of regeneration procedures as well. Three breakthrough innovations are illustrated by the following U.S. Patents: 5,986,158 (novel process and regeneration procedures), 6,855,856 (catalyst with optimized porosity and particle size), and 8,163,969 (alkylation process with an improved catalyst), all granted to Albemarle (inventors - E.H. van Broekhoven et al.). Other solid acid technologies use a less robust catalyst that still contains leachable components.

Reactor and Process design

The AlkyClean solid acid alkylation process operates in the liquid phase at moderate operating conditions, so no refrigeration, as used in the case of sulfuric acid alkylation, is required. The general process scheme is similar to that employed by both HF and H_2SO_4 alkylation processes with respect to the recycling of isobutane back to the reactors. However, in the case of the AlkyClean process, the reactors contain fixed bed catalyst and are designed to keep olefin concentration low and I/O at the active sites of the catalyst high. In this way hydrogen transfer reactions leading to the desired products are favored as described in the Chemistry Section.

Regeneration procedures

Regeneration of the catalyst is carried out continuously by cyclic switching from olefin addition (alkylation), to addition of dissolved hydrogen (mild regeneration), without changing reactor conditions. Nevertheless, depending on the severity, overall olefin conversion may drop, hence a higher temperature regeneration with hydrogen is carried out every week or so. This restores catalyst activity and selectivity and also distinguishes AlkyClean technology from other developments.

Demonstration Plant Operation

The final Basis of Design was developed and optimized at Neste's Porvoo facility during the time period 2002-2004. All elements of the technology (catalyst, process, regeneration, hardware, etc.) were fully demonstrated and proven.

Figure 2. Photograph of the Zibo Haiyi Plant

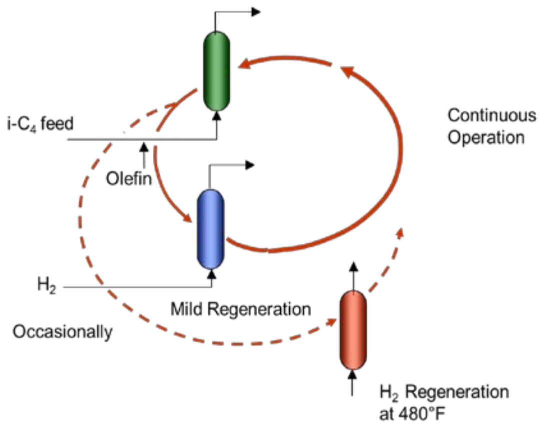

Figure 3. AlkyClean Flow Scheme.

Commercial Scale AlkyClean Unit Start-up

The first commercial-scale, solid catalyst alkylation unit was started up on August 18, 2015, at Zibo Haiyi Fine Chemical Co., LTD (Haiyi). The unit, which employs CB&I's AlkyClean technology, jointly developed by CB&I, Albemarle Catalysts and Neste Oil, has a capacity of 2,700 BPSD of alkylate production (100,000 kta). The unit is located in Zibo, Shandong Province, Peoples Republic of China and has achieved all performance expectations. In addition, the octane value (RON) of the alkylate product has been consistently measured between 96 and 98, quite high when compared with typical alkylate products. The value of alkylate, as a gasoline blend component, increases with higher RON value.

AlkyClean technology uses Albemarle's AlkyStar catalyst, a robust zeolite catalyst, and together with CB&I's novel reactor scheme, high-quality alkylate product can be produced without the use of liquid acid catalysts in the manufacturing process.

Cross-media effects

Since no corrosive media are present, cost of maintenance and repair of the AlkyClean process will be much lower and reliability much higher. This will reduce emissions of hydrocarbons during such periods of time. Catalyst needs replacement only once every five years. The spent catalyst contains zeolite, alumina matrix and a very low concentration of Pt metal; consequently it is relatively harmless and can easily be transported off site for the reclamation of Pt. The noble metal is reused, while solids can be utilized in the construction industry.

Capital investment and operating costs

Capital investment requirements for the AlkyClean process were optimized by CB&I as process licensor. The results indicate that the total installed cost is somewhat higher than an equivalent H_2SO_4 unit, not unexpected when the value proposition for the refiner is the elimination of liquid acid catalyst by a true solid catalyst. The total cost of catalyst and utilities for the AlkyClean process is also somewhat higher than that of H_2SO_4 technology, but we expect to achieve lower costs in the future as we further optimize the plant design.

Existing liquid acid units may be revamped to AlkyClean technology by reusing the existing feedstock pretreatment and distillation facilities and replacing the reaction section. Since AlkyClean technology creates no waste water or acid sludge, no acid neutralization facilities are required which eliminates related costs.

Product properties and yield

The alkylate product from the AlkyClean process meets all specifications (e.g. RON, vapor pressure and end boiling point) for reformulated gasoline blend stock. In addition, the new “green” technology does not produce heavy polymeric side products, while HF and H_2SO_4 technologies form acid-soluble oils waste with this material, which must be incinerated. So the alkylate yield from the AlkyClean process is at least as high as found in conventional liquid acid processes.

IV CONCLUSIONS

In conclusion, the AlkyClean technology has been proven at a commercial scale since August 2015 and is available to refinery operators that want or need an inherently safer technology when compared with conventional liquid acid catalyzed alkylation technologies.

Additional environmental benefits have also been demonstrated with the elimination of waste materials that are typically generated with conventional liquid acid alkylation technologies. Furthermore, alkylate quality and yields are comparable.